NATIONAL BUREAU OF STANDARDS REPORT

7792

HEATS OF FORMATION OF METALLIC BORIDES
BY FLUORINE BOMB CALORIMETRY

Eugene S. Domalski
George T. Armstrong

PROGRESS REPORT FOR THE PERIOD
1 OCTOBER 1962 to 31 JANUARY 1963

TO

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

1 February 1963

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

Functions and Activities

The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

Publications

The results of the Bureau's research are published either in the Bureau's own series of publications or in the journals of professional and scientific societies. The Bureau publishes three periodicals available from the Government Printing Office: The Journal of Research, published in four separate sections, presents complete scientific and technical papers; the Technical News Bulletin presents summary and preliminary reports on work in progress; and the Central Radio Propagation Laboratory Ionospheric Predictions provides data for determining the best frequencies to use for radio communications throughout the world. There are also five series of nonperiodical publications: Monographs, Applied Mathematics Series, Handbooks, Miscellaneous Publications, and Technical Notes.

A complete listing of the Bureau's publications can be found in National Bureau of Standards Circular 460, Publications of the National Bureau of Standards, 1901 to June 1947 ($1.25), and the Supplement to National Bureau of Standards Circular 460, July 1947 to June 1957 ($1.50), and Miscellaneous Publication 240, July 1957 to June 1960 (includes Titles of Papers Published in Outside Journals 1950 to 1959) ($2.25); available from the Superintendent of Documents, Government Printing Office, Washington 25, D.C.

NATIONAL BUREAU OF STANDARDS REPORT

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Heat Measurements Section
Heat Division

PROGRESS REPORT FOR THE PERIOD
1 OCTOBER 1962 to 31 JANUARY 1963

TO

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
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Delivery Order (33-616)61-09
Task No. 3048-30482 EFFORT

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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ABSTRACT

Recent analytical work on α-$A\ell B_{12}$, γ-$A\ell B_{12}$ and $A\ell B_2$ are given. Various tasks dealing with the construction, alteration, and replacement of apparatus are discussed. The energy equivalent of the calorimeter has been determined using benzoic acid as a reference standard.

Introduction

The following was accomplished on Delivery Order (33-616)61-09 for the period 1 October 1962 to 31 January 1963: (1) analytical work on α-$A\ell B_{12}$, γ-$A\ell B_{12}$ and $A\ell B_2$ has been completed, (2) various tasks have been performed dealing with construction, alteration and replacement of apparatus required in preparing for the calibration of the calorimeter and subsequent fluorine combustion experiments of the aluminum borides, (3) the energy equivalent of the calorimeter has been determined using benzoic acid as a reference standard.

Analytical Data on the Aluminum Borides

The Carborundum Company has supplied us with two samples of γ-$A\ell B_{12}$; one, 63.6 grams of large crystals several mm. in diameter, the other, 49.2 grams of -80 mesh granules crushed from the large crystals. The large crystals have a black metallic luster, while the granules appear reddish-brown. According to the technical staff at the Carborundum Company in charge of supplying these materials, it is doubtful whether the pure γ-phase can exist without about 10% of the α-phase present. The γ-$A\ell B_{12}$ phase appears to be syntactically intergrown with the α-$A\ell B_{12}$ phase.

The analytical results obtained for the γ-$A\ell B_{12}$ sample are as follows:

Theoretical for γ-$A\ell B_{12}$	Aluminum	17.22%
	Boron	82.78%

Observed:

γ-$A\ell B_{12}$ Crystals

		% Aluminum	% Boron
		16.32	80.55
		16.33	80.54
		16.38	

% Magnesium	% Calcium	% Carbon
0.095	0.011	0.14
		0.16

γ-$A\ell B_{12}$ Powder

		% Aluminum	% Boron
		16.01	80.83
		16.05	80.59

% Iron	% Magnesium	% Calcium	% Carbon
0.005	0.088	0.007	0.08
0.005			0.06

X-ray diffraction analysis on the γ-$A\ell B_{12}$ powder gave a pattern identical to α-$A\ell B_{12}$, as is to be expected.

The following are the results of carbon analysis on α-$A\ell B_{12}$, for which the remainder of the analysis was previously reported.

	% Carbon
α-$A\ell B_{12}$ crystals	0.22
	0.16
α-$A\ell B_{12}$ powder	0.12
	0.10

The analytical data presented in the last progress report (NBS Report 7725, 1 October 1962, page 5) gives results found for total aluminum and total boron in aluminum diboride as found by our Applied Analytical

Chemistry Section and by the Carborundum Company analysts.

Source	% Aluminum	% Boron
Theoretical for AlB_2	55.51	44.49
The Carborundum Company	54.74	44.29
NBS Applied Analytical Chemistry Section	53.00	47.04

Inspection of the above values shows a significant difference in the results found for total aluminum and total boron in aluminum diboride by our analysts and those at Carborundum. In an attempt to resolve this disparity, copies of the analytical procedures used in the Applied Analytical Chemistry Section on aluminum diboride and α- and γ-aluminum dodecaboride were sent to Carborundum so that a comparison of procedures could be made. Further, a small amount of the same sample that was analyzed here was sent to Carborundum so that its composition could be checked. A few weeks later, a telephone reply was received from Carborundum informing us that the NBS analyses on aluminum diboride were correct and that the error lay in some approximations used in their analytical procedures. The fact that the total boron analysis was greater than the theoretical value was ascribed to lattice vacancies and/or boron atoms in aluminum positions.

Subsequent analysis of aluminum diboride for small impurities has shown the following:

% Copper	% Iron	% Silicon
0.74	0.023	0.022
0.76	0.022	0.030
	0.030	

% Magnesium	% Calcium	% Manganese	% Carbon
0.024	0.016	< 0.01	0.06
0.023	0.011	< 0.01	0.07
			0.11

An x-ray powder pattern obtained for aluminum diboride by our Constitution and Microstructure Section is in good agreement with data available on this phase. Study of the pattern gave no evidence for the presence of any other phase. The lattice constants found are in good agreement with the literature cited.

Lattice Constants:

(E. J. Felton, J. Am. Chem. Soc. 78, 5977-8 (1956).)

$a = 3.009$ A, $c = 3.262$ A

(NBS Constitution and Microstructure Section)

$a = 3.005$ A, $c = 3.250$ A

Experimental

A. Construction, Alteration and Replacement of Apparatus

Various improvements were made to the vacuum system used in conjunction with the fluoride manifold. Its performance was tested and it was found to maintain 0.1 micron of Hg, which is considered satisfactory.

An oxygen bomb loading station was constructed for the purpose of filling combustion bombs. In essence, the station consists of a cylinder of high purity oxygen, a regulating valve, a cupric oxide furnace, maintained at 450°C, an ascarite trap, a pressure gage, and a thermostatted brass block to hold the combustion bomb.

Stainless steel tubing ($\frac{1}{4}$ in. OD, 0.035 in. wall thickness) was used to join the high purity fluorine cylinder to the manifold. Also part of the system is a large tower containing activated sodium fluoride. The latter is used to absorb any hydrogen fluoride that may be present in the fluorine as an impurity.

Defective valves in the fluorine manifold were replaced, restoring the apparatus to its normal operating condition.

The feet on the bottom of the nickel combustion bomb were increased in length from 3/16 in. to 11/16 in. in order to improve water circulation under the bomb during a heat measurement. A bomb handle, which is a permanent part of the bomb's screw cap, was constructed to facilitate the entry and removal of the bomb from the calorimeter.

A constant flow device was constructed for the cooling water used to counteract the energy input of the thermoregulator, and thereby improve the temperature regulation of the calorimeter jacket.

B. <u>Energy Equivalent Experiments</u>

Because of certain changes made to the calorimeter system, it was considered advisable to recalibrate the calorimeter at this time using benzoic acid as a reference standard. Six benzoic acid calibration experiments were made in a nickel combustion bomb using 30 atm. of high purity oxygen, a platinum crucible, a two cm. platinum fuse wire (0.004 in. diam.), and one ml. of distilled water. The mass of benzoic acid used (1.70 grams) gave about a three degree temperature rise. The nitric acid titration usually made at the conclusion of a combustion experiment could be neglected because high purity oxygen was used.

The energy equivalent for the standard calorimeter was found to be 146,930 joules ohm^{-1} $\pm$13 joules ohm^{-1}, where the uncertainty is the standard deviation of an individual experiment.

U. S. DEPARTMENT OF COMMERCE
Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D. C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research. Crystal Chemistry.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Polymers. Macromolecules: Synthesis and Structure. Polymer Chemistry. Polymer Physics. Polymer Characterization. Polymer Evaluation and Testing. Applied Polymer Standards and Research. Dental Research.

Metallurgy. Engineering Metallurgy. Microscopy and Diffraction. Metal Reactions. Metal Physics. Electrolysis and Metal Deposition.

Inorganic Solids. Engineering Ceramics. Glass. Solid State Chemistry. Crystal Growth. Physical Properties. Crystallography.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials. Metallic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Far Ultraviolet Physics. Solid State Physics. Electron Physics. Atomic Physics. Plasma Spectroscopy.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Elementary Processes. Mass Spectrometry. Photochemistry and Radiation Chemistry.

Office of Weights and Measures.

BOULDER, COLO.

Cryogenic Engineering Laboratory. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

CENTRAL RADIO PROPAGATION LABORATORY

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Systems. Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Frequency Utilization. Modulation Research. Antenna Research. Radiodetermination.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. High Latitude Ionosphere Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

RADIO STANDARDS LABORATORY

Radio Physics. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Radio Plasma. Millimeter-Wave Research.

Circuit Standards. High Frequency Electrical Standards. High Frequency Calibration Services. High Frequency Impedance Standards. Microwave Calibration Services. Microwave Circuit Standards. Low Frequency Calibration Services.

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